Environmental assessment of thermo-chemical processes for bio-ethylene production in comparison with bio-chemical and fossil-based ethylene

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ABSTRACT

The use of biomass for production of chemicals is gaining interest because of its potential to contribute towards a reduction in greenhouse gas emissions and other environmental benefits linked to the substitution of fossil resources. But, conversely to biofuels, studies focusing on environmental impacts of biomass-derived chemicals are scarce. This paper uses life cycle assessment to evaluate the environmental sustainability of bio-ethylene from poplar produced by the following three thermo-chemical routes: direct and indirect dehydration of ethanol and production of olefins via dimethyl ether. The indirect route is the best option for most impact categories for all three allocation methods considered: system expansion, economic and energy basis. However, the dimethyl ether-to-olefins route has the lowest global warming potential. In comparison to ethylene produced bio-chemically from sugar beet, the thermo-chemical indirect route has lower impacts for all categories except human, terrestrial and freshwater toxicities. All three thermo-chemical alternatives show a significant reduction in global warming potential (up to 105% in the case of dimethyl ether-to-olefins) and depletion of fossil fuels when compared to conventional ethylene production from fossil fuels. However, the results also suggest that bio-ethylene produced by any of the three thermo-chemical routes would lead to a significant increase in most other impact categories relative to fossil fuels. Therefore, while trying to reduce greenhouse gas emissions, the overall environmental sustainability of bio-ethylene suffers from the increase in other environmental impacts.

1. Introduction

The European chemicals industry is committed to a gradual increase in the utilization of renewable feedstocks, with the objective of producing 25% of biomass-derived chemicals in 2030 (DSBC, 2012). Biomass-derived chemicals act as a storage of biogenic carbon (Haro et al., 2014) and could potentially have negative net greenhouse gas emissions (The Royal Society, 2016). This makes them an appealing target for reducing the impact on climate change from the chemicals industry. Among the candidates for producing bio-chemicals, ethylene stands out as the largest chemical commodity with the global demand of 150 million tonnes in 2016 (Mitsubishi Chemical, 2017). Ethylene is currently largely produced by steam cracking using different hydrocarbon feedstocks (ethane, propane, naphtha and gas oils), although the use of ethane is being favoured, especially in Europe (Ethylene Profile, 2015).

Even though bio-ethylene production is still far from playing an important role in the near future, it can complement production of fossil-based olefins (Amghizar et al., 2017; Braskem Company, 2017). Compared to other biomass-derived chemicals, the production of bio-ethylene has an advantage that it can be introduced directly into existing value chains, infrastructure and markets (Arvidsson, 2016). Ethylene can be produced from biomass following two different pathways: bio-chemical and thermo-

chemical. In the former, ethanol produced from the fermentation of sugars is dehydrated into ethylene. The Brazilian company Braskem is already producing 200,000 t/y of polymer-grade bio-ethylene using sugarcane bio-ethanol as an intermediate (Braskem Company, 2017).

In the thermo-chemical pathway, lignocellulosic biomass is converted into ethylene prior to thermal treatment (pyrolysis and/ or gasification) and further chemical conversion of produced syngas into ethylene. There are two alternatives for the chemical conversion, either the production of methanol/dimethyl ether (DME) or ethanol as chemical intermediates. In the case of methanol/DME, a methanol-to-olefins reactor is used. For ethanol, the same dehydration process as in the bio-chemical pathway is utilized. Several studies have evaluated techno-economic feasibility of ethylene production via the bio-chemical route, including Kamzon et al. (2016), Becerra et al. (2017) and Nitzsche et al. (2016). Equivalent studies of thermo-chemical pathways have also been carried out (Haro et al., 2013; McKechnie et al., 2015; Sharifzadeh et al., 2015). In this study, we focus on the thermo-chemical route to evaluate the environmental sustainability of producing bio-ethylene from biomass. The results are compared with bio-chemical ethylene produced by dehydration of first-generation bio-ethanol and with ethylene obtained by steam cracking of fossil resources. The following three main alternative pathways are considered: direct ethanol dehydration, indirect ethanol dehydration and DME-to-olefins. Therefore, the scope of the work covers the most promising alternatives for bio-ethylene production via thermo-chemical conversion (Haro et al., 2013).

In contrast to biofuels, there are scarce examples of life cycle assessment (LCA) studies of biomass-derived chemicals. Most existing studies are focused on specialty chemicals produced via the bio-chemical pathway (e.g. Fiorentino et al., 2017) and only a few on chemical commodities like ethylene (e.g. Cheali et al., 2015). Studies of life cycle impacts of ethylene production using the thermo-chemical pathway are rare and the number of impacts considered is limited. For example, Karka et al. (2017) considered only three categories: cumulative energy demand, global warming potential and water consumption. A couple of other studies discussed the key environmental issues in the production of bio-ethylene focusing on second-generation ethanol (Belboom and Léonard, 2016; Liptow et al., 2013). First-generation bio-chemical ethanol was studied by Ghanta et al. (2014) who considered corn as a feedstock in a US context while Tsiropoulos et al. (2015) evaluated the use of sugarcane in Brazil and India. Sugarcane from Brazil was also considered by Kikuchi et al. (2017) for the production of ethanol in Japan, alongside the use of domestic sugarcane-molasses. Other studies assessed the economic and environmental implications of using bio-ethanol for ethylene production instead of utilizing it as a transportation fuel (McKechnie et al., 2015; Posen et al., 2015). Finally, Horváth et al. (2017) analysed the carbon efficiency of the conversion of bio-ethanol into different chemicals, including ethylene.

Therefore, there is a lack of comprehensive studies of environmental impacts of thermo-chemical production of ethylene from biomass. This study aims to fill this knowledge gap. The results are compared to the impacts from ethylene produced by bio-chemical conversion as well as with ethylene produced from fossil feedstocks to provide a comprehensive multi-criteria analysis of the environmental performance of bio-ethylene. As far as we are aware, this is the first study of its kind internationally.

2. Methodology

The study involves a comparative attributional LCA, based on the guidelines of the ISO 14040/44 standards (2006a, 2006b). The goal and scope of the study are described next, followed by the inventory data and an overview of the impact assessment method used in the study.

2.1. Goal and scope

The main goal of the study is to estimate and compare life cycle environmental impacts of the three alternative methods for producing bio-ethylene from biomass via thermo-chemical conversion: direct ethanol dehydration (Case 1); indirect ethanol dehydration (Case 2); and DME to olefins (Case 3). A further goal is to compare these thermo-chemical routes with ethylene produced from first-generation ethanol via the bio-chemical route and with ethylene from fossil-based resources.

As indicated in Fig. 1, the scope of the study is from 'cradle to gate', with two main stages considered: biomass supply (cultivation, collection and transportation to the processing plant); and production of bio-ethylene and its co-products. The use of bio-ethylene and the co-products, as well as their distribution, are excluded from the system boundaries. The construction and decommissioning of the production plant are also excluded as the impacts of infrastructure per unit of product are negligible over the (long) lifespan of industrial plants (Reyes Valle et al., 2015).

The functional unit is defined as the production of 1 tonne of ethylene.

2.2. System description

The plant size chosen is equivalent to 500 MWth in terms of the energy content of the feedstock processed, based on the higher heating value (HHV). This plant size is typically considered in studies of biomass-to-liquids (BTL) plants (Villanueva et al., 2011). The type of biomass processed in the plant is the same for each of the three cases considered. However, the amount of biomass required per tonne of ethylene produced and the output of the co-products vary depending of the production route due to the different efficiency and selectivity of the three routes. The feedstock is poplar as detailed in the next section.

2.2.1. Feedstock supply
Poplar is selected as the feedstock, which has recently attracted significant interest as an energy crop (Guo et al., 2014). The production plant is assumed to be based in the Duero Valley (*Castilla y León*, Spain) as there is extensive cultivation of poplar there due to favourable climatic conditions. For these reasons, land use change is not considered.

The life cycle of a poplar crop spans 16 years. In the first year, land preparation and the planting of cuttings take place. This is followed by three tree-growing cycles of five years each (Gasol et al., 2009), with the trees being cut to the ground after each cycle. At the end of the third cycle, the trunks are treated with insecticide to remove the roots and, after three months, new cuttings are planted. The average production of biomass is 216 t/ha on a dry basis for the three cycles as a whole. Further description of the feedstock supply can be found in Reyes Valle et al. (2015).

2.2.2. Case 1: direct ethanol dehydration
This process involves three main steps:

i) bioslurry production from biomass (Fig. 2);
ii) production of ethanol from bioslurry by direct route through gasification and catalytic conversion of syngas (Fig. 3); and
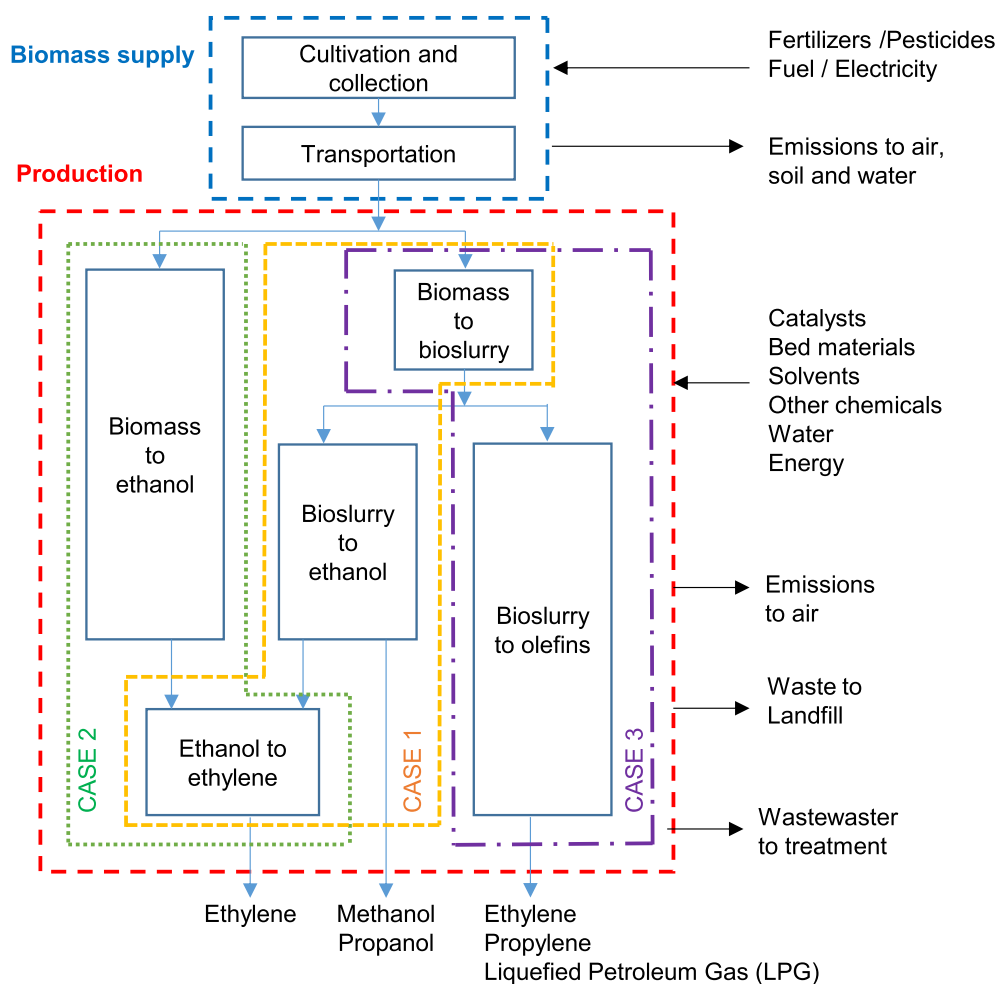
Fig. 1. Systems boundaries considered for the production of bio-ethylene via the thermo-chemical route. (Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether to ethylene.).
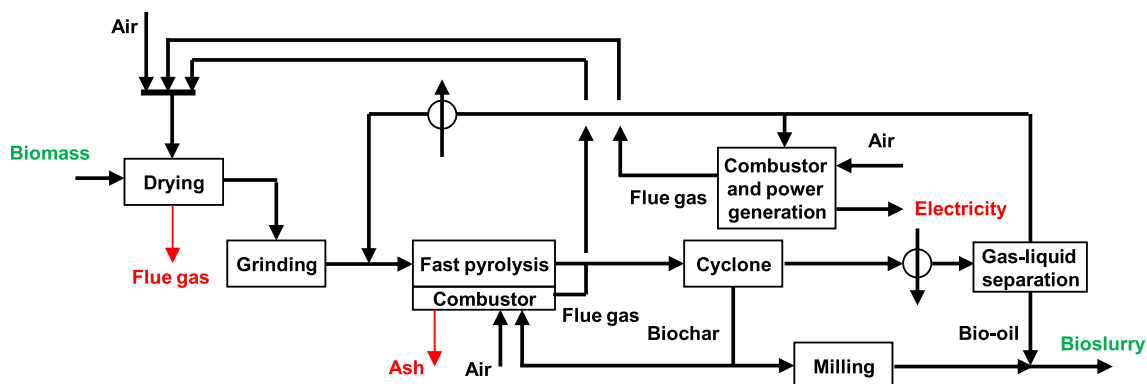

Fig. 2. Bioslurry production used in the direct ethanol dehydration route (Case 1) and in the DME-to-olefins route (Case 3). (Adapted from Villanueva et al. (2011). The green colour refers to the main input and output from the process. The red colour signifies the outputs from the process, including co-products. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

iii) production of ethylene by ethanol dehydration (Fig. 4), based on a commercial technology (Chematur Engineering AB, 2017).

A detailed description of this route is given in the Supporting Information (SI).

2.2.3. Case 2: indirect ethanol dehydration

In this case, there are two main stages:

i) production of ethanol from biomass by indirect route; and
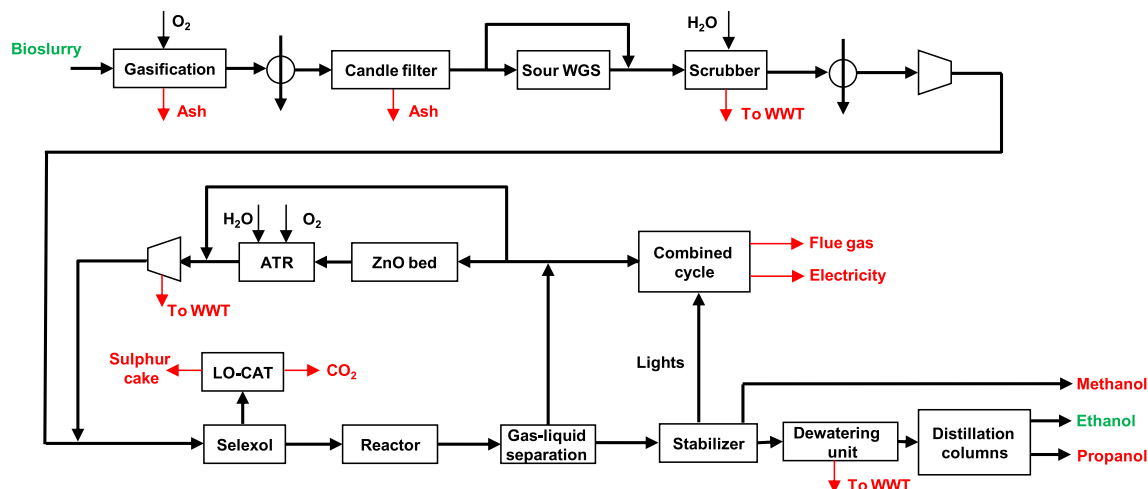ii) production of ethylene by ethanol dehydration.

Fig. 3. Ethanol production via the direct route (Case 1). (Adapted from Villanueva et al. (2011). WGS: water-gas shift; WWT: wastewater treatment; ATR: autothermal reformer; LO-CAT: liquid-phase oxidation catalytic unit. The green colour refers to the main input and output from the process. The red colour signifies the outputs from the process, including co-products. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. Ethylene production by dehydration of ethanol. (Adapted from Villanueva et al. (2011). WWT: wastewater treatment. The green colour refers to the main input and output from the process. The red colour signifies the outputs from the process, including co-products. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
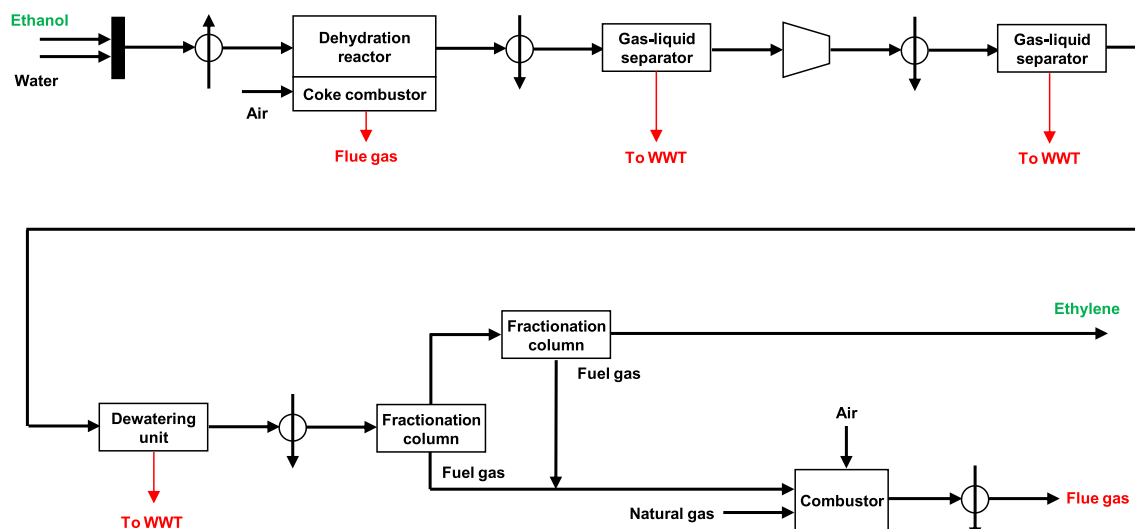
i) The process for producing ethanol is detailed in Fig. 5 (Haro et al., 2012). It follows the following sequence: first, a fraction of the syngas is used for methanol synthesis; the methanol is then dehydrated to DME and water; and finally, DME and the rest of the syngas are reacted to produce ethanol via methyl acetate. Methanol is also produced in this last step. For further details, see the SI.

ii) The production of ethylene follows the same process as in Fig. 4.

2.2.4. Case 3: DME to olefins
Case 3 comprises two main steps:

i) bioslurry production; and
ii) production of olefins.

The bioslurry and the olefins are produced in the processes

outlined in Figs. 2 and 6 (Haro et al., 2013), respectively. A detailed description is provided in the SI.

2.3. Life cycle inventory

All background LCA data have been obtained from the Ecoinvent database V3.3 (Moreno Ruiz et al., 2016), except for NPK fertilizers, which have been sourced from the agri-footprint database (Durlinger et al., 2014). The 2016 Spanish electricity mix has been considered in the analysis (REE, 2017). The storage of biogenic carbon is not included since the end-use of ethylene is not considered and it is not known how long the carbon would be stored before being released back to the atmosphere. However, the influence of carbon storage on the results is discussed in section 3.3.

2.3.1. Biomass supply
The inventory data for the biomass supply stage are summarised in Table 1. The data refer to the annual production of 1 Mt of
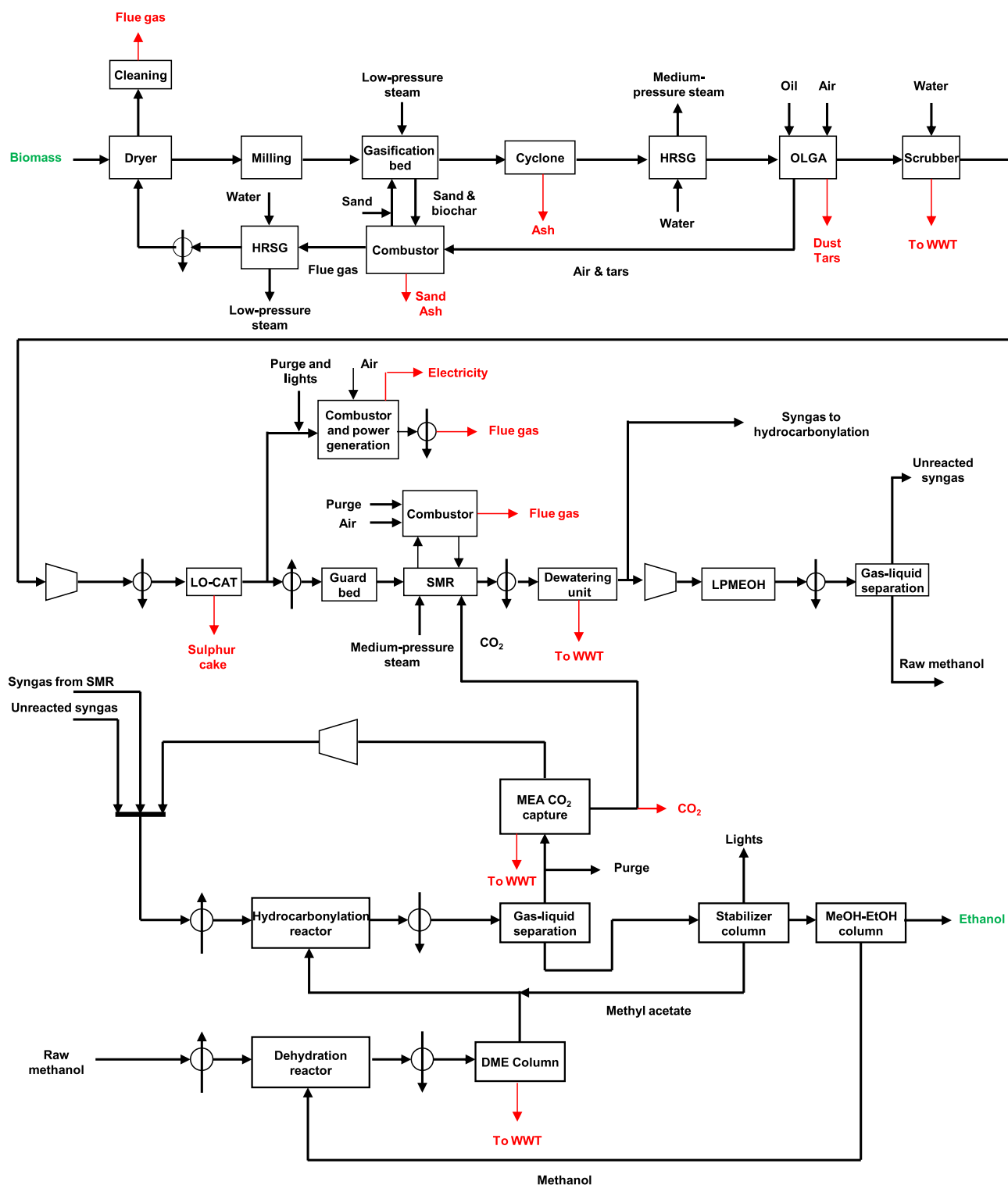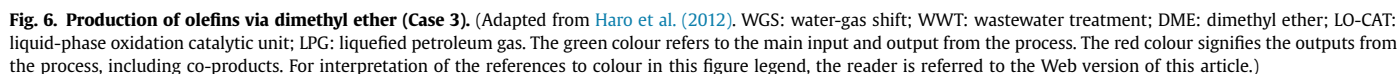
Fig. 5. Ethanol production via the indirect route (Case 2). (Adapted from Haro et al. (2012). HRSG: heat recovery steam generator; LPMEOH: liquid-phase methanol; LO-CAT: liquid-phase oxidation catalytic unit; SMR: steam methane reformer; MEA: monoethanolamine; DME: dimethyl ether. The green colour refers to the main input and output from the process. The red colour signifies the outputs from the process, including co-products. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

biomass (wet) needed for the chosen size of the ethylene plant (equivalent to the HHV of the feedstock of 500 MWth). The requirements for fertilizers, pesticides, diesel, electricity and the transport have been calculated following the biomass supply model described in Reyes Valle et al. (2015). The amounts of pesticides and

their emissions to soil have been calculated according to Nemecek and Schnetzer (2012) and Sutter (2010). Emissions to water have been estimated using the average lixiviation fractions given in Franke et al. (2013). The concentration of metals in the fertilizers for the lixiviation calculations and the emissions to air from the use of

Fig. 6. Production of olefins via dimethyl ether (Case 3). (Adapted from Haro et al. (2012). WGS: water-gas shift; WWT: wastewater treatment; DME: dimethyl ether; LO-CAT: liquid-phase oxidation catalytic unit; LPG: liquefied petroleum gas. The green colour refers to the main input and output from the process. The red colour signifies the outputs from the process, including co-products. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

fertilizers have been determined using data and methodologies proposed in Nemecek and Schnetzer (2012). According to these authors, the nutrients supplied to the soil are assumed to be taken up by the biomass or lost to the air or water, so the quantity of nutrients in the soil should not change in the long term. Therefore, no emissions to the soil from the use of fertilizers are considered.

2.3.2. Ethylene production

The inventory data for the production stage are summarised in Table 2 for the three production routes considered. These data have been obtained through simulation in Aspen Plus (Haro et al., 2012, 2013; Villanueva et al., 2011). The simulations are based on the best available data from existing commercial (i.e. dehydration stage) and experimental plants. It can be seen from Table 2 that, for the same plant size (500 MWth), the requirements for biomass and the type and amount of co-products per tonne of ethylene are different for each route.

2.3.3. Allocation

As the ethylene production system produces several co-products, it is necessary to allocate the environmental burdens

between them. As shown in Table 2, the co-products in each case are:

- Case 1: methanol, propanol and sulphur cake;
- Case 2: sulphur cake; and
- Case 3: liquefied petroleum gas (LPG), propylene and sulphur cake.

Following the ISO 14040/44 guidelines (ISO, 2006a, 2006b), system expansion has been applied first. However, a sensitivity analysis is included, considering energy and economic allocation, to explore the effect on the results of the allocation approach and ensure the robustness of the conclusions. For system expansion, the system has been credited for avoiding the production of the above co-products in other production systems; the data for these production systems have been sourced from Ecoinvent. For energy and economic allocation, the impacts have been allocated between ethylene and the co-products based on their HHV values and market prices in 2014, respectively; these values can be found in Table 3. The proportion of environmental burdens allocated to ethylene is summarised in Table 4. The economic value of sulphur

Table 1
Life cycle inventory data for annual production of 1 Mt (500 MWth) of poplar (wet).

Category	Sub-category	Amount
Fertilizers	NPK (9-18-27)	6098 t/y
	N fertilizer (ammonium nitrate)	2541 t/y
Pesticides	Metil pirimifos (insecticide)	6 t/y
	Gliphosate (herbicide)	50 t/y
	Propineb (fungicide)	4 t/y
Diesel		843 t/y
Electricity		20 MWh/y
Emissions to air	Diesel emissions[a]	
	Carbon dioxide	2630 t/y
	Carbon monoxide	9.58 t/y
	Methane	0.14 t/y
	NMVOC[b]	4.36 t/y
	Nitrous oxide	0.1 t/y
	Nitrogen oxides	37.11 t/y
	Particulates	3.77 t/y
	Sulphur dioxide	0.85 t/y
	Ammonia	16.8 kg/y
	Polycyclic aromatic hydrocarbons	2.8 kg/y
	Ammonia[c]	47 t/y
	Nitrous oxide[c]	24 t/y
	Nitrogen oxides[c]	5 t/y
Emissions to water	Nitrate	615 t/y
	Phosphate	11 t/y
	Cadmium	13 kg/y
	Copper	51 kg/y
	Zinc	306 kg/y
	Lead	20 kg/y
	Nickel	59 kg/y
	Chromium	195 kg/y
Emissions to soil	Metil pirimifos[d]	6 t/y
	Gliphosate[d]	50 t/y
	Propineb[d]	4 t/y
Transport	Feedstock to the production plant	$1.4 \cdot 10^7$ t km/y

[a] Emissions from the combustion of diesel in the machinery.
[b] Non-methane volatile organic compounds.
[c] Emissions from the use of fertilizers.
[d] Active components: $C_{11}H_{20}N_3O_3PS$ (metil pirimifos); $C_3H_8NO_5P$ (glyphosate); $C_5H_8N_2S_4Zn$ (propineb).

cake is considered negligible because it is suitable for agricultural purposes but is undesirable as a chemical feedstock (NREL, 2006). Similarly, as it is not used for energy purposes due to the high water content, its HHV has not been considered. Hence, no burdens have been allocated to this co-product. However, the system has been credited for displacing the sulphur fertilizer.

2.3.4. Comparison with other production routes and sources of ethylene

To put the results in perspective, the environmental impacts of thermo-chemical bio-ethylene are compared with two alternatives: ethylene from fossil resources and from ethanol made using first-generation crops. The former is currently the main source of ethylene, produced via steam cracking of hydrocarbons (Mohsenzadeh et al., 2017). For bio-ethanol, the most prevalent feedstock in Europe is sugar beet (Clifford, 2017). Muñoz et al. (2014) reported that sugar beet had the lowest environmental impacts for ethanol production via fermentation in comparison with other feasible crops in Europe, such as maize and wheat. Hence, this feedstock has been considered for the comparison. The inventory data for both fossil and sugar beet-derived ethylene have been sourced from Ecoinvent. The data for ethanol dehydration have been obtained through process modelling as described in section 2.2.2.

2.4. Impact assessment

The SimaPro v.8.3. software (Pré Consultants B.V., 2017) has been used for the life cycle modelling and the impacts have been calculated following the CML 2 method (Guinée et al., 2001), using the April 2016 update. All 11 impacts included in the CML 2 method have been considered: abiotic depletion potential of elements ($ADP_{elements}$), abiotic depletion potential of fossil fuel resources (ADP_{fossil}), global warming potential (GWP), ozone depletion potential (ODP), human toxicity potential (HTP), freshwater aquatic ecotoxicity potential (FAETP), marine aquatic ecotoxicity potential (MAETP), terrestrial ecotoxicity potential (TETP), photochemical oxidants creation potential (POCP), acidification potential (AP) and eutrophication potential (EP).

3. Results and discussion

This section compares the environmental impacts of the three routes considered, first for system expansion and then for the energy-based and economic allocation. This is followed by comparison with the production of ethylene using first-generation bio-ethanol and steam cracking of fossil resources.

3.1. Comparison of thermo-chemical routes for system expansion

As shown in Fig. 7, when system expansion is applied, Case 2 (indirect ethylene dehydration) is the best option for eight out of 11 impacts considered. This is despite the credits for avoiding the production of sulphur fertilizer being negligible. The reason for its superior performance is the lower consumption of biomass and electricity per tonne of bio-ethylene produced compared to Cases 1 and 3 (see Table 2). For the remaining three impacts (ADP_{fossil}, GWP and ODP), Case 3 (DME to olefins) is the preferred alternative.

The ethylene production stage is the main contributor to the impacts for all three routes for ten out of the 11 impact categories. The exception is the bioslurry production with almost a negligible contribution because this stage is energy self-sufficient and no chemicals or catalysts are used. Only for the TETP is the biomass supply a major contributor because of the use of pesticides. The contribution of the agricultural stage is generally lower in Case 2 across the impacts due to the higher ethylene production per tonne of biomass.

For all three cases, the use of catalyst metals, such as Mo, Cu and, to a lesser extent, Zn and Ni, is the highest contributor to $ADP_{elements}$. As can be observed in Fig. 7, Case 2 is the best option for this impact. The reason for that is that ethanol synthesis in Case 2 is based on non-metallic catalyst (H-mordenite). In Case 2, 62% of the impact is from the use of Mo in the Co–Mo catalyst in the guard bed for reducing the sulphur concentration. Most of the impact in Case 1 (93%) comes from Mo in the S_2Mo catalyst used in the synthesis reactor and in the Co–Mo catalyst of the sour water-gas shift reactor. Finally, for Case 3, 87% of the impact is related to Zn–CuO catalyst in the DME synthesis reactor.

Cases 1 and 3 have lower values for ADP_{fossil}, GWP and ODP than Case 2 due to the system credits for avoiding the production of their respective co-products in other processes. Case 3 is the best option with the negative net values for these three categories: −62.4 GJ/t (ADP_{fossil}), −0.07 t CO_2 eq./kg (GWP), and −59 mg CFC-11 eq./t (ODP). Propanol is the main source of the credits for ADP_{fossil} (94%), GWP (98%) and ODP (96%) in Case 1. In Case 3, credits are mainly coming from Propylene for ADP_{fossil} (74%) and GWP (85%), and from LPG for ODP (almost 100%). Without considering the system credits, electricity is responsible for most of the impacts in Case 3, with contributions of 67%–78% for these three impacts. In Case 1, these three impacts are from electricity (49%–60%) and from natural gas in the ethanol dehydration stage (18%–28%). Finally, in Case 2, the main contributors to these three categories are natural gas used in

Table 2
Life cycle inventory data for bio-ethylene production expressed per tonne of ethylene produced.

Category	Sub-category	Unit per tonne ethylene	Case 1: Direct ethanol dehydration	Case 2: Indirect ethanol dehydration	Case 3: Dimethyl ether to olefins
Biomass	Poplar wood (wet)	kg	15,847	8636	16,889
Catalysts	Alumina	kg	0.20	0.35	—
	Co—Mo	kg	0.11	0.07	0.12
	Cu/ZnO	kg	—	0.03	—
	CZA/HZSM-5	kg	—	—	8.4
	H-Mordenite	kg	—	0.20	—
	Nickel	kg	0.02	0.03	—
	S_2Mo	kg	0.52	—	—
	ZnO	kg	0.54	0.70	—
	Zeolite	kg	—	—	4.2
Bed materials	Sand	kg	—	10.95	—
	Zeolite	kg	0.24	0.07	0.03
Solvents	DEPG[a]	kg	2.37	—	1.60
	Monoethanolamine	kg	—	3.74	—
	Diesel	kg	—	35.82	—
Other chemicals	KOH	kg	0.02	0.02	0.03
	Methanol	kg	—	—	0.38
	Oxygen	kg	8511	—	8423
	NaOH	kg	—	0.03	—
Water	Power generation	kg	1900	10,017	1904
	Process	kg	2365	31,458	866
Energy	Electricity[b]	MWh	1.7	0.39	2.1
	Natural gas	Nm^3 [c]	84.0	84.0	—
Emissions to air	CO biogenic	kg	352	0	137
	CO fossil	kg	0.06	0.06	—
	CO_2 biogenic	kg	14,813	292	—
	CO_2 fossil	kg	179	9452	14,795
	SO_2	kg	0.58	—	0.47
	SO_3	kg	0.01	—	—
Solid waste to landfill[d]	Biomass (chippings)	kg	396	216	422
	Ash	kg	100	65	106
	Spent catalysts	kg	4.20[d]	1.42[d]	14.48[d]
	Spent bed materials	kg	0.24	0.07	0.03
Wastewater to treatment		kg	12,373	28,586	12,018
Co-products	Methanol (>98%)	kg	469	—	—
	Propanol (>98%)	kg	182	—	—
	Liquefied petroleum gas	kg	—	—	357
	Propylene (>99.5%)	kg	—	—	871
	Sulphur cake (70% water)	kg	3.59	2.45	3.85
Total production	Ethylene (>99.5%)	t/y	65,966	121,048	61,896

[a] DEPG: dimethyl ethers of polyethylene glycol.
[b] Net energy consumption after subtracting the total electricity consumed from the electricity produced.
[c] Nm^3: normal cubic meter at standard pressure and temperature.
[d] 1.20 kg (Case 1), 1.02 kg (Case 2) and 8.48 kg (Case 3) of which is hazardous waste.

Table 3
Values used for energy and economic allocation.

Output	Co-product (kg/t ethylene)	HHV[a] (MJ/kg)	Price (€/t)
Ethylene	—	50.2	1000[b]
Methanol	469	22.6	275[b]
Propanol	182	33.6	3750[b]
Propylene	871	48.8	1050[b]
LPG	357	49.6[c]	862[d]

[a] Aspen (2007).
[b] ICIS Pricing Data (2014).
[c] Based on liquefied petroleum gas (LPG) composition (% wt): 2.9% ethylene, 28.8% ethane, 18.5% propane, 2.8% propylene and butenes
[d] Regulated price in Spain (BOE, 2014).

ethanol dehydration (29%—40%), electricity (20%—25%) and the diesel used as the sorbent in the OLGA process for biochar removal and then subsequently burned in the biochar combustor (17%—23%). The lower consumption of electricity in Case 2 (0.39 MWh/t) relative to Cases 1 and 3 (1.7 and 2 MWh/t) is because ethanol production is energy self-sufficient, with all the electricity (and natural gas) consumed in Case 2 supplied from the ethanol dehydration stage.

Case 2 is the best option for HTP, FAETP and MAETP. As mentioned earlier, this is due to the lower consumption of electricity, metal catalysts and pesticides, the latter related to the lower use of biomass per unit of product compared to Cases 1 and 3. The

Table 4
Percentage of environmental impact allocated to bio-ethylene.

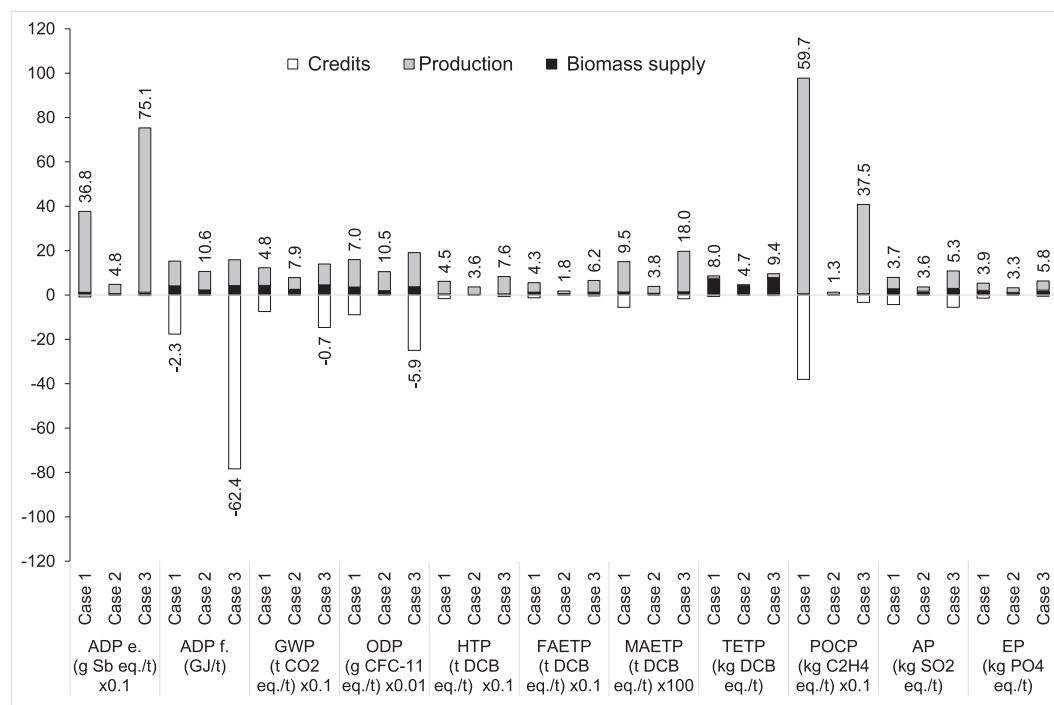| Allocation basis	Case 1: Direct ethanol dehydration	Case 2: Indirect ethanol dehydration	Case 3: Dimethyl ether to olefins
Energy	75.0%	100%	45.5%
Economic	55.2%	100%	45.0%

Fig. 7. Life cycle environmental impacts of bio-ethylene produced via three thermo-chemical routes for system expansion. (Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. The values shown on top of each bar represent the total impact after the system credits have been applied. Some impacts have been scaled to fit. To obtain the original values, multiply by the factor shown on the x-axis for the relevant impacts. ADP e.: abiotic depletion potential of elements, ADP f.: abiotic depletion potential of fossil resources, GWP: global warming potential, ODP: ozone layer depletion potential, HTP: human toxicity potential, FAETP: freshwater aquatic ecotoxicity potential, MAETP: marine aquatic ecotoxicity potential, TETP: terrestrial ecotoxicity potential, POCP: photochemical oxidants creation potential, AP: acidification potential, EP: eutrophication potential).

main contributors to these impacts in Case 2 are MEA used for CO_2 capture (66% of HTP), pesticides (32% of FAETP) and electricity (55% of MAETP). For Case 1, electricity is responsible for 25% of HTP, 17% of FAETP and 50% of MAETP. The use of the molybdenum catalyst in the synthesis reactor and the guard bed contributes 38%–48% to the three toxicity impacts and the use of pesticides 19% to FAETP. In Case 3, electricity contributes 20%–59% to these impacts categories. The use of the Cu–ZnO catalyst is responsible for 27%–49% while 17% of FAETP is due to the use of pesticides in the feedstock. Although Case 2 has lower HTP than Cases 1 and 3, the main reason for this impact are carcinogenic substances, specifically, ethylene oxide emitted in the manufacturing process of MEA.

The agricultural stage is the major contributor to TETP in all three cases (>80%). Almost all of the impact (98%) derives from the use of pesticides. Case 2 is the best option because of the lower amount of biomass required per tonne of ethylene produced.

Case 2 is also the best option for POCP. Cases 1 and 3 have a much higher impact (46 and 29 times, respectively), almost all of which is due to the higher CO emissions associated with the Selexol process. This impact is higher for Case 1 than Case 3 because the gas flow in the Selexol process is higher for the former as it includes the recirculation stream of the synthesis loop in addition to the raw synthesis gas stream.

Finally, Case 2 is also the best option for AP and EP. This is due to the lower electricity consumption and biomass requirements than in Cases 1 and 3. The main contributors to EP in Case 2 are the make-up water used in the steam power cycle (30%), fertilizers (29%) and electricity consumption (17%). Fertilizers and electricity also cause 30% and 33% of AP. In Case 1, 52% of the AP and 37% of the EP are related to electricity consumption. The use of fertilizers adds a further 24% and 32%, respectively. Similarly, for Case 3, electricity and the fertilizers are responsible for 60% and 28% of AP and 48% of

19% of EP, respectively.

Further details on the contribution to the impacts of different categories (shown in Table 2) can be found for each production route in Tables S1-S3 in the SI.

3.2. Sensitivity analysis of allocation approaches

If the environmental burdens are allocated on the energy basis (Fig. 8), Case 2 is the best option for five impacts ($ADP_{elements}$, FAETP, MAETP, POCP and AP) and Case 3 for three (ADP_{fossil}, GWP and ODP). Three other categories (HTP, TETP and EP), which are similar for these two options, are also lower than for Case 1, which in turn is the worst alternative for ten out of 11 categories considered.

For allocation on the economic basis (Fig. 9), Case 2 has the lowest impacts for the same five categories as for energy allocation ($ADP_{elements}$, FAETP, MAETP, POCP and AP). These values are the same as for the energy allocation as there are no co-products with energetic or economic value in Case 2. For Case 3, the impacts for economic and energy allocation are almost identical because, by coincidence, the allocation factors are very similar (45.5% and 45%; see Table 4). Case 3 is again the best option for ADP_{fossil}, GWP and ODP. On the other hand, all impacts for Case 1 show a 26% reduction with respect to energy allocation. This is due to the allocation factors changing from 75% to 55% for the economic allocation. This change is a consequence of the higher price of propanol with respect to ethylene (3750 €/t of propanol vs 1000 €/t of ethylene) while ethylene has a higher HHV value (50.2 MJ/kg vs 33.6 MJ/kg for propanol). Case 1 is still the worst option for POCP. Case 2 is the least preferred alternative for three categories (ADP_{fossil}, GWP and ODP) while Case 3 has the highest $ADP_{elements}$. Cases 1 and 2 have the highest impacts with similar values for FAETP, MAETP and AP.
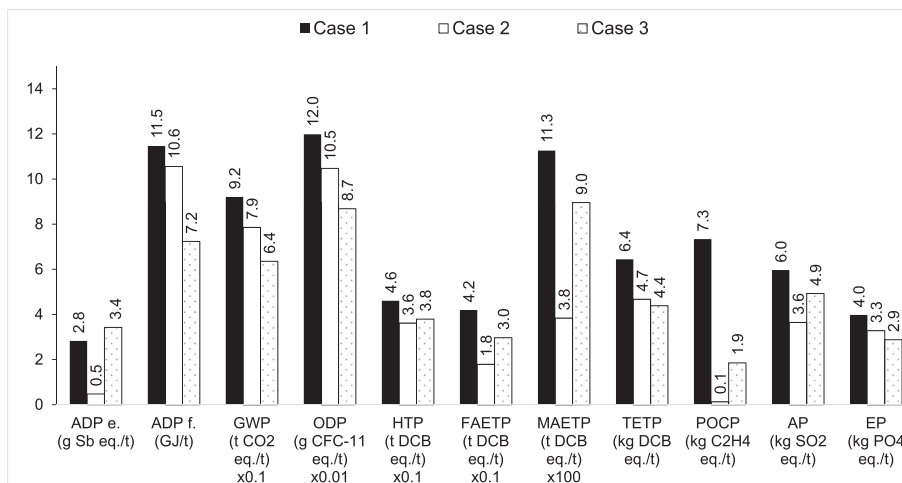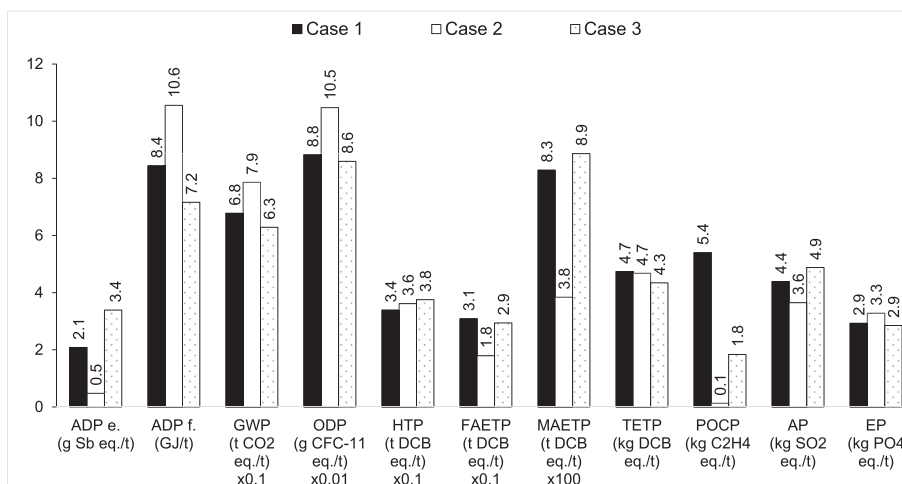
Fig. 8. Life cycle environmental impacts of bio-ethylene produced via three thermo-chemical routes for allocation on the energy basis. (Energy basis: higher heating value. Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. For the impacts nomenclature, see Fig. 7. Some impacts have been scaled to fit. To obtain the original values, multiply by the factor shown on the x-axis for the relevant impacts.).

Fig. 9. Life cycle environmental impacts of bio-ethylene produced via three thermo-chemical route for allocation on the economic basis. (Economic basis: market prices of ethylene and the co-products. Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. For the impacts nomenclature, see Fig. 7. Some impacts have been scaled to fit. To obtain the original values, multiply by the factor shown on the x-axis for the relevant impacts.).

For the remaining three categories (HTP, TETP and EP), all three cases have similar values.

Case 2 is ranked top for five impacts (ADP$_{elements}$, FAETP, MAETP, POCP and AP) and Case 3 for three (ADP$_{fossil}$, GWP and ODP) regardless of the method used. Case 2 is also the top ranked alternative for HTP for system expansion and energy allocation, while Case 1 is the best option for economic allocation. For the remaining two impacts (TETP and EP), the top ranking position for system expansion changes from Case 2 to Case 3 if energy or economic allocation is used.

Therefore, the sensitivity analysis of allocation approaches shows that, while the absolute values of the impacts change, the allocation method has little influence on the best-ranking options. Thus, it can be concluded that the results are robust with respect to different allocation methods.

3.3. Comparison of thermo-chemical and bio-chemical ethylene

Fig. 10 shows that, for system expansion, the bio-chemical route using sugar beet as the feedstock for ethanol, is a better option than the thermo-chemical route for only three impacts across the three cases considered: HTP, FAETP and TETP. For the remaining eight impacts, it is less sustainable than at least one of the thermo-chemical cases.

The higher ADP$_{fossil}$, GWP and ODP for the bio-chemical route than any of the three thermo-chemical cases are due to the heat demand in the biological reactor, supplied mainly by fossil-fuel resources, and the higher specific biomass consumption per tonne of ethylene involving higher diesel consumption in the agricultural activities. GWP is also higher due to the higher emissions of nitrous oxide from the use of fertilizers. The higher values of AP and EP are related respectively to the higher emissions of ammonia to air and nitrate to water from the use of fertilizers for sugar beet than for poplar.

For ADP$_{elements}$, MAETP and POCP, bio-chemical ethylene has higher impacts than Case 2 but lower than Cases 1 and 3. For ADP$_{elements}$, the higher impact than for Case 2 is due to the higher consumption of pesticides and biocides for the sugar beet and the higher biomass requirement per unit of ethylene produced. The lower impact with respect to Cases 1 and 3 is related to their
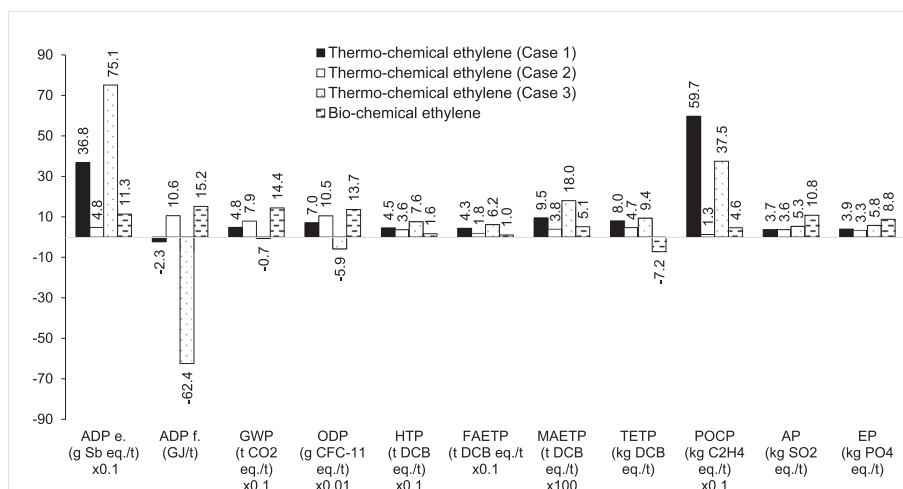
Fig. 10. Comparison of thermo-chemical and bio-chemical bio-ethylene for system expansion. (Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. Bio-chemical ethylene: dehydration of ethanol produced from sugar beet by fermentation. For the impacts nomenclature, see Fig. 7. Some impacts have been scaled to fit. To obtain the original values, multiply by the factor shown on the x-axis for the relevant impacts.).

utilization of metal catalysts. The higher MAETP and POCP relative to Case 2 is due to the heat consumed in the fermentation reactor. Cases 1 and 3 show higher values for MAETP and POCP because of the higher electricity consumption and CO emissions from Selexol, respectively.

3.4. Comparison of thermo-chemical bio-ethylene and fossil-based ethylene

Compared to ethylene from fossil resources, thermo-chemical bio-ethylene reduces ADP_{fossil} by 84%−196% and GWP by 66%−105% across the three cases considered (Fig. 11). These results are not surprising given the use of biomass for bio-ethylene. Furthermore, the electricity consumption per unit ethylene produced is lower for bio-ethylene (0.39−2.1 MWh/t; see Table 2) than for its fossil-based equivalent (3.5−6.8 MWh/t (Deloite, 2013)). In addition, the reduction in these two impacts is greater for Cases 1 and 3 due to the credits for the co-products.

The reduction in GWP would be much higher if the biogenic carbon storage in bio-ethylene was considered, due to the carbon sequestration by the feedstock. If all the carbon contained in 1 tonne of bio-ethylene is considered as stored carbon, 3.14 t CO_2 eq./t would need to be subtracted from the GWP values shown in Fig. 9 for each of the three routes. In that case, the GWP would range from −3.21 t CO_2 eq./t for Case 3 to −2.36 t CO_2 eq./t for Case 2. However, these potential savings in GHG should be interpreted with caution as processing of ethylene into an end product would lead to additional GHG emissions and, depending on the type of the product and its longevity, potential release of the stored carbon back to the atmosphere.

Extrapolating the results (without considering biogenic carbon) to the global levels, and assuming that 20% of the demand of 150 Mt/y (Mitsubishi Chemical, 2017) is supplied by thermo-chemical bio-ethylene, would lead to the reductions in GWP shown in Fig. 12. These reductions have been calculated considering the current supply of fossil-based ethylene. For system
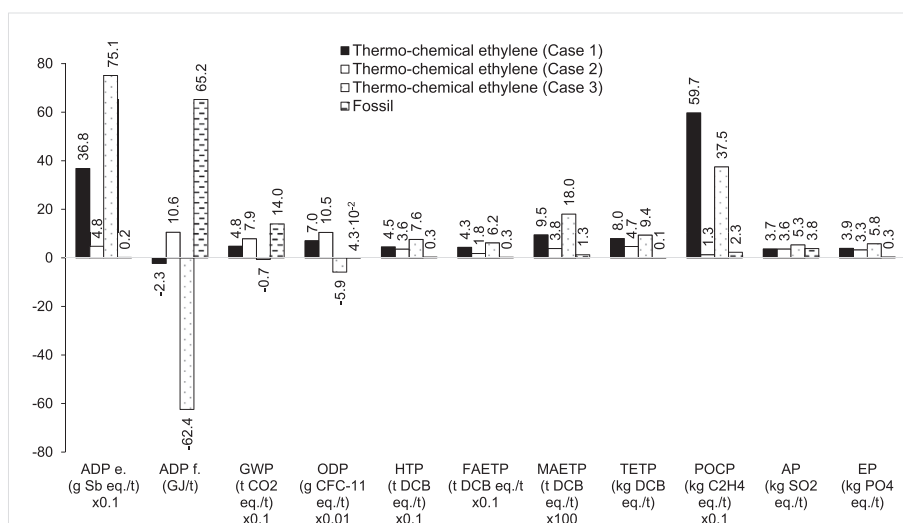

Fig. 11. Comparison of thermo-chemical bio-ethylene and fossil-based ethylene for system expansion. (Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. Fossil: steam cracking. For the impacts nomenclature, see Fig. 7. Some impacts have been scaled to fit. To obtain the original values, multiply by the factor shown on the x-axis for the relevant impacts.).

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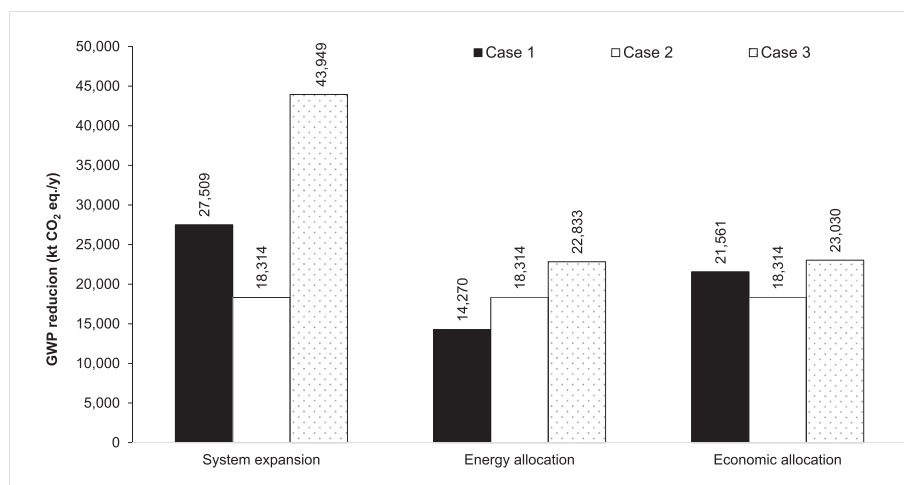

Fig. 12. Reduction in global warming potential (GWP) assuming 20% of the global demand was supplied by thermo-chemical bio-ethylene instead of fossil-based ethylene.
(The rest of the demand supplied by ethylene produced by steam cracking. Case 1: direct ethanol dehydration; Case 2: indirect ethanol dehydration; Case 3: dimethyl ether (DME) to olefins. For the impacts nomenclature, see Fig. 7.).

expansion, the savings would range from 18,300 kt CO_2 eq./y in Case 2 to 43,950 kt CO_2 eq./y in Case 3. The latter is higher than the annual CO_2 eq. emissions of Sweden in 2015 (JRC, 2017). These savings would be reduced by almost two times for the energy and 22%–48% for the economic allocation for Cases 1 and 3 (there would be no change for Case 2 due to insignificant credits for the sulphur as fertilizer).

However, six other impacts would be higher for bio-ethylene than its equivalent produced by steam cracking (Fig. 11): $ADP_{elements}$, HTP, FAETP, MAETP, TETP and EP. These impacts would increase from three (MAETP) to 39 times ($ADP_{elements}$) due to the use of metal catalysts, pesticides, fertilizers and MEA which are not required in the production of ethylene from fossil resources. For POCP, Cases 1 and 3 have higher POCP values than fossil-based ethylene (16 and 3.5 times, respectively) because of the CO emissions from the Selexol process. However, the fossil option has a higher impact than Case 2 due to methane leakage from the equipment, pipes, etc. (Berdowski et al., 1995). Furthermore, ODP is higher for Cases 1 and 2 (17 and 25 times) but Case 3 has a 14.6 times lower impact due to the system credits. Finally, Cases 1 and 2 have a similar AP to the fossil option, which is lower than the value in Case 3. These impacts could be reduced by developing more efficient catalysts with longer lifespans. This would reduce the biomass requirements per tonne of ethylene and reduce the amount of both the catalyst needed and solid waste generated at the end of its useful lifetime.

In summary, switching from fossil to bio-ethylene would lead to substantial reductions in GWP but would also increase significantly a number of other impacts. This is congruent with the results in Liptow et al. (2015), who reported lower GWP and POCP but higher EP and AP for bio-ethylene from wood produced via thermochemical route (methanol to olefins) compared to ethylene from fossil resources. Case 3 offers the greatest potential for reducing GWP (105%) but it also has higher impacts for six other categories. Case 2 also provides a considerable reduction in GWP (44%) but shows a lower or no increase in other categories compared to ethylene from fossil resources.

4. Conclusions

This paper has discussed the environmental performance of three thermo-chemical processes for ethylene production from a

lignocellulosic feedstock: direct and indirect dehydration of ethanol and dimethyl (DME)-to-olefins route. Three approaches have been considered for apportioning the impacts among the co-products: system expansion, and energy and economic allocation.

When system expansion is applied, the indirect route (Case 2) has the lowest values for eight out of the 11 impact categories ($ADP_{elements}$, HTP, FAETP, MAETP, TETP, POCP, AP and EP), mostly because of the lower requirement of biomass, catalysts and electricity per unit of bio-ethylene produced. On the other hand, the DME-to-olefins route (Case 3) has the lowest impacts for GWP, ADP_{fossil} and ODP due to the system credits for the co-products. Similar conclusions regarding the best alternative are reached when energy or economic allocation is applied. The main difference with the results from system expansion is that the direct dehydration route (Case 1) is the worst option for most of the impact categories for energy allocation due to the lower energy content of the co-product methanol compared to ethylene.

Compared to bio-chemical ethylene produced from sugar-beet ethanol, the indirect route reduces the impacts by 23%–73% for most categories, except for HTP, FAETP, and TETP. The other two thermo-chemical routes have lower ADP_{fossil}, ODP, GWP and, to a lesser extent, AP and EP. However, bio-chemical ethylene is the best option for FAETP, HTP and TETP, POCP and $ADP_{elements}$.

All the thermo-chemical processes offer a great potential for reducing GWP (44%–105%) and ADP_{fossil} (104%–196%) relative to ethylene produced from fossil resources. However, for most of the other categories, bio-ethylene has higher impacts. Therefore, the substitution of ethylene produced from fossil fuel resources with thermo-chemical bio-ethylene to reduce greenhouse gas emission could result in an increase in other environmental impacts.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2018.08.147.

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